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The global aims of this research program have been to understand the surface chemistry of materials having important applications in tribology and to understand the influence of adsorbate structure on the frictional properties of metal-metal interfaces. The materials chosen for study have been those used as boundary layer additives to lubricant mixtures. Boundary layer additives are usually amphiphilic species present in low concentrations in lubricant fluids whose role is to form surfactant-like monolayers on metal surfaces. These monolayers form the last barrier to metal - metal contact when two surfaces are in contact under sufficiently high loads that all the fluid lubricant has been squeezed out of the contact region. For the most part our work has concentrated on the fluorinated alcohols, acids and fluorinated alkyl groups on metal surfaces. In addition we have begun the study of fluorinated ether surface chemistry.

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SURFACE SPECIES IN TRIBOLOGY

Final Technical Report

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CONTENTS

1. PROJECT GOALS

The global aims of this research program have been to understand the surface chemistry of materials having important applications in tribology and to understand the influence of adsorbate structure on the frictional properties of metal-metal interfaces. The materials chosen for study have been those used as boundary layer additives to lubricant mixtures. Boundary layer additives are usually amphiphilic species present in low concentrations in lubricant fluids whose role is to form surfactant-like monolayers on metal surfaces. These monolayers form the last barrier to metal - metal contact when two surfaces are in contact under sufficiently high loads that all the fluid lubricant has been squeezed out of the contact region. For the most part our work has concentrated on the fluorinated alcohols, acids and fluorinated alkyl groups on metal surfaces. In addition we have begun the study of fluorinated ether surface chemistry.

The interest in the fluorocarbon surface chemistry stems from the fact that the perfluoro-alkylether (PFAE) fluids have important potential applications as high temperature lubricant fluids but are limited by an absence of materials suitable for use as boundary layer additives. Furthermore, although the fluorinated ethers themselves have inherently high thermal stability some forms are known to decompose in the presence of metal surfaces. The details of this surface chemistry are unknown. In

general the surface chemistry of fluorocarbons has received little attention and so we started our work by studying a couple of fluorinated species for which the surface chemistry of their hydrocarbon analogues is well understood. These are the alkoxides, alkyls groups and carboxylates.

At this point our work has given us an extremely clear understanding of the role that fluorine plays in influencing the reaction kinetics of a number of species adsorbed on metal surfaces. This work is summarized in the following sections. Its implications are twofold. The comparison of reaction kinetics between hydrocarbons and fluorocarbons has given us a means to probe the electronic structure of the transition states for these reactions. From a purely scientific perspective this is extremely exciting since very little is known about the transition states for any surface reactions. From a more practical perspective we have been able to control the decomposition of a number of boundary layer type species and understand what approaches should be taken to increase thermal stability in these species.

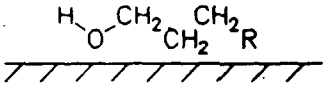
2. Alcohol Adsorption on Metal Surfaces

During the course of this program we have made substantial progress in understanding the growth of thin molecular films of alcohols on Ag(110), Cu(100) and Cu(111) surfaces. These films are to be used as model boundary films with which we can modify the frictional properties of surfaces. Using thermal desorption measurements we have been able to determine that on all three surfaces the straight chain alcohols adsorb reversibly. At monolayer and submonolayer coverages the alcohols desorb with first order kinetics. At coverages in excess of one monolayer a second desorption peak appears at lower temperatures. This second peak results from desorption of condensed alcohol and exhibits zero-order kinetics. From these spectra the heats of adsorption of the monolayer have been determined as listed in Table I for the Ag(110) surface. The results are quite similar on the Cu surfaces.

TABLE I. Alcohol heats of Adsorption on the Ag(110) Surface

Alcohol	Multilayer Heat of Desorption	Monolayer Heat of Desorption
Methanol	8.4 kcal/mole	9.7 kcal/mole
Ethanol	9.3	10.7
Propanol	9.8	11.9
Butanol	11.0	12.8
Pentanol	11.9	14.1

The heat of adsorption of the alcohol on the surface is incremented by 1.1 kcal/mole per methylene unit in the alkyl chain. This number is roughly the incremental heat of interaction that one observes between alkyl chains in alkanes as they are increased in length. The same basic desorption behavior has been observed on the other surfaces. Additional characterization of these surface films has made use of work function measurements, and vibrational spectroscopy and X-ray photoemission spectroscopy. Vibrational spectra of the monolayer alcohol films show that the OH bond is still intact but highly perturbed. The OH stretch frequency in methanol is shifted from $\sim 3700\ cm^{-1}$ in the gas phase down to $\sim 3300\ cm^{-1}$ when adsorbed on the surface. Similarly the OH bending mode is shifted from its gas phase value indicating that the molecules are adsorbed through the oxygen atom. The remainder of the spectrum is not greatly perturbed from that of the gas phase molecule. Our current picture of the adsorption of these species on the surface is that they adsorb through the oxygen atom with their alkyl chains oriented parallel to the metal surface.



As models for potential boundary layer additives to the perfluoro-alkylether lubricants we have worked with several fluorinated alcohols. These are commercially

available compounds which have been fluorinated beginning at the C2 position and are the analogues of ethanol (CF_3CH_2OH), propanol ($CF_3CF_2CH_2OH$) and butanol ($CF_3CF_2CF_2CH_2OH$). We have studied their surface chemistry on Ag(110), Cu(100) and Cu(111) surface using thermal desorption measurements and vibrational spectroscopy. There has been virtually no prior work with fluorinated species on metal surfaces and none with these compounds. For the most part the chemistry that we have observed using the fluorinated alcohols on the clean surfaces mimics the chemistry that has been observed using the straight chain alcohols. There is apparently some difference between the adsorption thermodynamics of the alcohols and their fluorinated analogues. Whereas the heat of adsorption of the alcohols is simply incremented by 1.1 kcal/mole by the addition of a methylene unit to the alkyl chain, the extension of the fluorinated alcohols from three to four carbon atoms results in a much smaller change in the heat of adsorption. The calculated heats of adsorption are given in Table II for the Ag(110) surface.

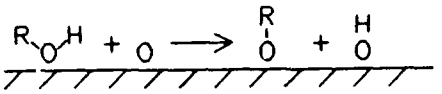
TABLE II. Heat of Adsorption for Fluorinated Alcohols on Ag(110)

Alcohol	Monolayer Heat of Adsorption
CF_3CH_2OH	11. kcal/mole
$CF_3CF_2CH_2OH$	11.9
$CF_3CF_2CF_2CH_2OH$	12.6

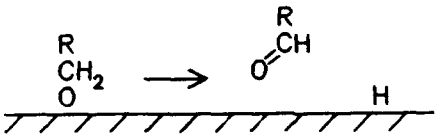
Again heat of adsorption appears to be dominated by the interaction of the OH group with the surface. The increment in the monolayer heat of adsorption resulting from the addition of a CF_2 unit to the chain is much smaller.

3. Alkoxide Decomposition on Metal Surfaces

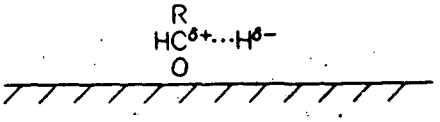
The chemistry of the alcohols on oxidized Ag(110), Cu(100) and Cu(111) surfaces is dramatically different from that observed on the clean surfaces. The oxide film at the surface participates in a reaction in which the alcohol is deprotonated to form a surface alkoxide species.



In the case of methanol adsorption the deprotonated species has been identified as the methoxide by spectroscopic work in a number of laboratories. The decomposition kinetics and products that we have observed serve to identify the higher molecular weight species as the straight chain alkoxides. The second product of this reaction is H_2O which desorbs from the surface at 190 K leaving the alkoxide monolayer. An interesting property of these monolayers is that they are much more stable on the surface than the molecular alcohols. Decomposition reactions occur in the range about 280K to 400K depending upon the surface used whereas desorption of the alcohols occurs in the temperature range 160 - 240 K. The alkoxides all decompose by a reation called β-hydride elimination which results in the production of an aldehyde.



The fluorinated alkoxides decompose at higher temperatures than their hydrogenated analogues. It is clear from the temperatures at which these are decomposing that fluorination of the alkyl group is stabilizing the surface intermediate. This is consistent with a decomposition mechanism in which the first step is hydride elimination passing through a transition state in which the C_β carbon atom is a cation.



The increasing electronegativity of the adjacent methyl group destabilizes the cationic transition state, thereby increasing the barrier to decomposition. The effect is quite

dramatic and the kinetic barriers to decomposition are listed in Table III for the Cu(100) surface.

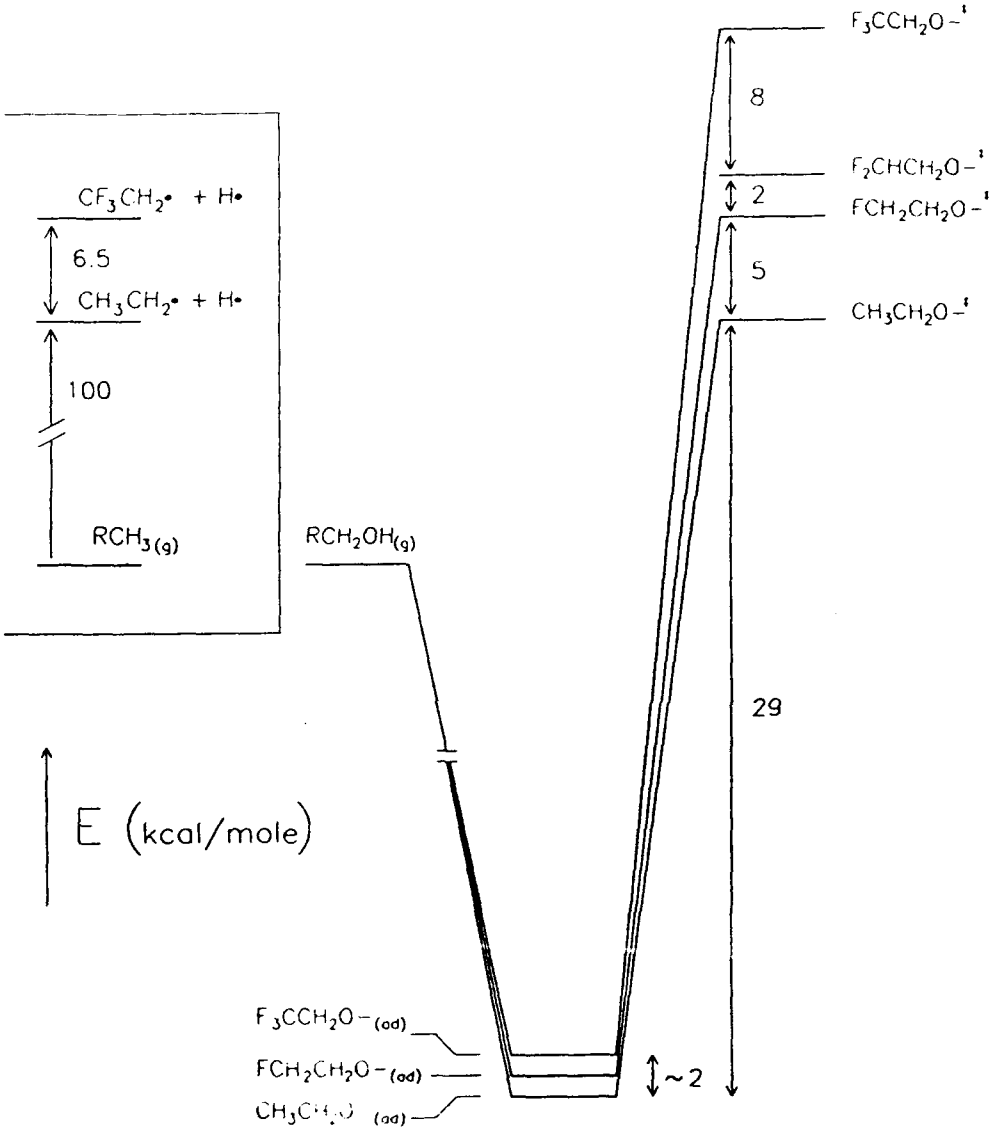
TABLE III. Decomposition temperatures and activation barriers for β-hydride elimination in alkoxides on the Cu(100) surface.

Alkoxide	Hydrocarbon			Fluorocarbon		
	T_{des} (K)	E_a (kcal/mole)	$log(\nu)$ (sec^{-1})	T_{des} (K)	E_a (kcal/mole)	$log(\nu)$ (sec^{-1})
Methoxide	400	30.3	16.2[a]			
Ethoxide	366	25.2	14.7[b]	507	42.2	17.8[c]
Propanoxide	372	25.6	14.7[b]	501	41.7	17.8[c]
Butanoxide	378	26.0	14.7[b]	506	42.1	17.8[c]
Pentanoxide	375	25.8	14.7[b]			

[a] Measured for methoxide on Cu(111) [13]
[b] Measured for ethoxide on Cu(111) [13]
[c] Measured for trifluoro-ethoxide on Cu(111) [13]

Alcohols adsorb on many metal surfaces in the form of alkoxides and β-hydride elimination is the elementary step initiating alkoxide decomposition to aldehydes. This is the reaction which ultimately leads to failure of boundary layer films formed of adsorbed alkoxides. We have made a series of systematic measurements of reaction kinetics and heats of ethoxide formation in order to fully understand the energetics of the decomposition process and the source of the increased thermal stability imparted by fluorination of the alkyl chain. The results of these measurements are shown in fig. 1. The heats of formation of the alkoxides from the gas phase alcohols are only weakly perturbed (< 0.5 kcal/mole) by fluorination of the alkyl chain. The barrier to β-hydride elimination on the other hand increases by 14 kcal/mole indicating that fluorination of the alkyl chain has an enormous destabilizing effect on the transition state for this surface reaction.

Fig. 1



Relative heats of formation of fluorinated ethoxides from gas phase ethanols and activation energies for β-hydride elimination in fluorinated ethoxides on the Cu(111) surface. The influence of fluorine on the transition state barrier is much greater than on the heat of formation of the ethoxides. The inset at the upper left illustrates the influence of CF_3 groups on the strengths of adjacent C-H bonds. The homolytic C-H bond strength in CF_3CH_3 is 6.5 kcal/mole greater than in CH_3CH_3.

The influence of fluorine can be understood in terms of the nature of the transition state for β-hydride elimination. Possible transition states are depicted in fig. 2. with the expected effect of fluorination of the methyl group. If the reaction is truly considered a β-hydride elimination in which the transition state has the form $C^{\delta+}\cdots H^{\delta-}$ then fluorination of the adjacent methyl group will result in destabilization of the transition state and an increase in the activation barrier as observed. By contrast the barrier to deprotonation ($C^{\delta-}\cdots H^{\delta+}$) would decrease since the trifluoro-methyl group would stabilize the anionic transition state. In the case of a homolytic bond breaking with no charge separation in the transition state the barrier is expected to go up slightly. In summary, the data that we have collected point towards a transition state for this reaction which is truly described as β-hydride elimination. It should be pointed out that the implications of this work extend far beyond decomposition of boundary layers in tribology since this reaction is important in catalytic dehydrogenation chemistry, olefin hydrogenation, and CVD reactions.

4. Branched Alkoxide Decomposition on Cu(111) Surfaces

Our understanding of the influence of fluorination on alkoxide decomposition kinetics also enables us to point to some fairly obvious candidates for forming stable alkoxide boundary layers from alcohols. Clearly, based on the types influence the we find fluorine to have on alkoxide stability we expect secondary fluorinated alcohols to be stable to much higher temperatures than the primary alcohols. Although the decomposition mechanism of the tertiary fluorinated alkoxides cannot be β-hydride elimination the stability of the tertiary alkoxides must exceed that of trifluoro-ethoxide. The decomposition of tertiary alkoxide must be initiated by C-F, C-C or C-O bond breaking. If these were to occur at low temperatures these reactions would be observed in the ethoxides. The barriers to these reactions must be greater than that of β-hydride elimination.

Recently we have measured the kinetics for decomposition of the secondary alkoxide on the Cu(111) surface. These are $(CH_3)_2CHO_{(ad)}$, $(CH_3)(CF_3)CHO_{(ad)}$ and $(CF_3)_2CHO_{(ad)}$ all of which decompose to yield acetone and fluorinated acetones.

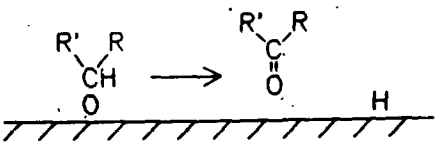


Fig. 2

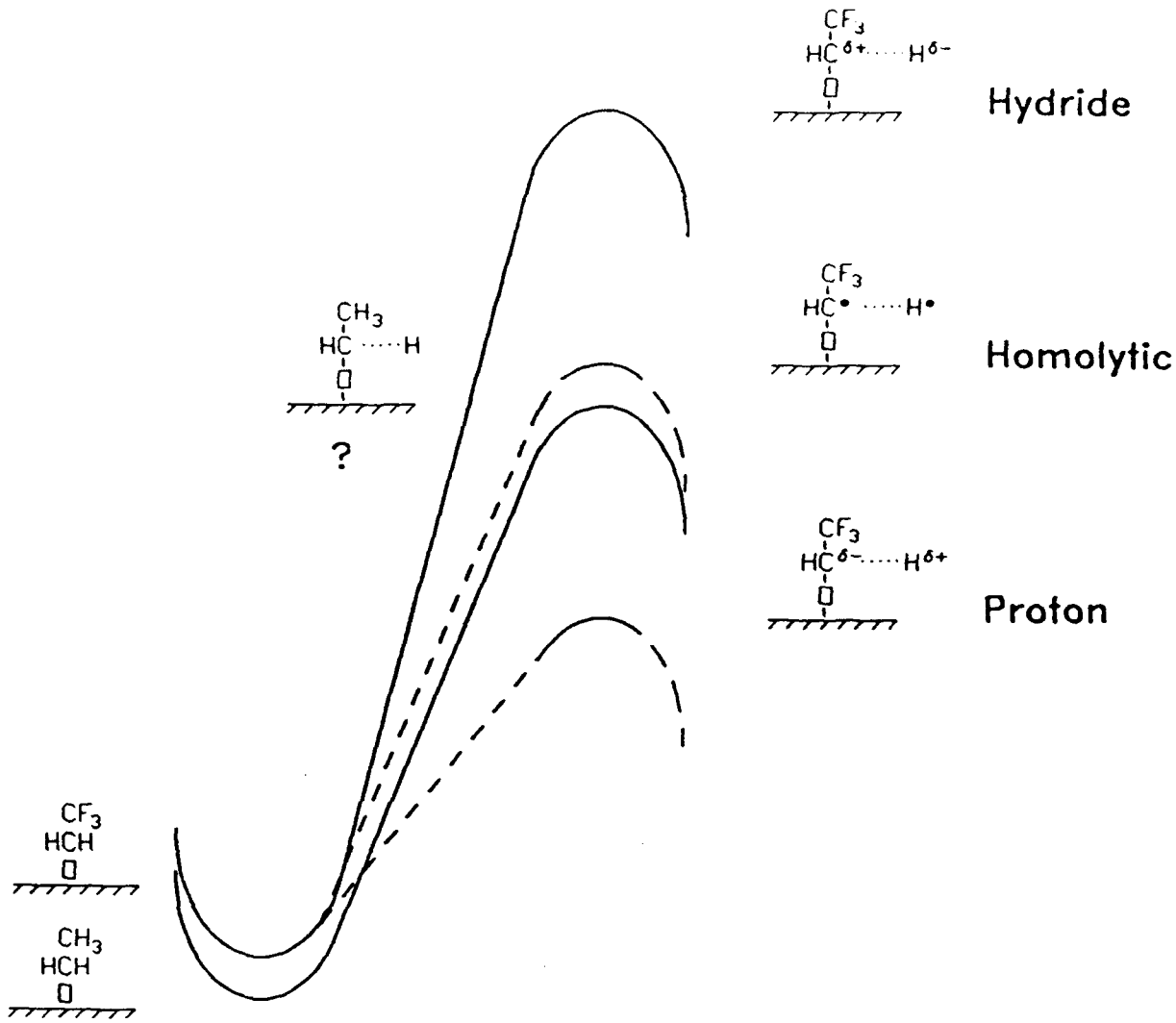


Illustration of possible transition states for decomposition of ethoxide to acetaldehyde and the influence of fluorine on the transition state energetics. The destabilization of the homolytic transition state is expected to be < 6.5 kcal/mole. The 13 kcal/mole increase in the activation barrier resulting from fluorination of the methyl group indicates that charge separation in the transition state leaves the β-carbon with net positive charge and the hydrogen atom with net negative charge.

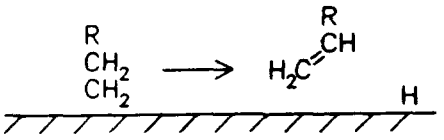
Table IV shows the decomposition temperatures and the activation energies for the decomposition. As expected, fluorination of the methyl groups greatly increase the thermal stability of these alkoxides.

TABLE IV. Decomposition Temperature and Barriers for Secondary Alkoxides on the Cu(111) Surface

Alkoxide	T_{dec}	E_a
$(CH_3)_2CHO-_{(ad)}$	400K	27 kcal/mole
$(CF_3)(CH_3)CHO-_{(ad)}$	490	42
$(CF_3)_2CHO-_{(ad)}$	580	63

5. Alkyl Group Decomposition on Cu(111) Surfaces

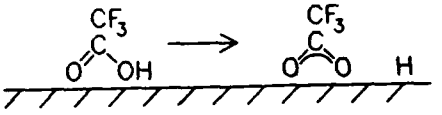
Our understanding of the surface chemistry of the alkoxides can be extended to an understanding of the chemistry of alkyl groups adsorbed on metals. In much the same way as fluorine influences the kinetics of alkoxide decomposition it can be expected to increase the barrier to β-hydride elimination in partially fluorinated alkyl groups. We have worked with propyl and 3,3,3-trifluoro-propyl groups on the Cu(111) surface. These can be formed by adsorption of propyl-iodide which decomposes at fairly low temperatures ($<$150K) to yield adsorbed iodine and propyl groups on the surface. The propyl groups then decompose at higher temperatures to give propylene (225K) and trifluoro-propylene (320K).



Propyl decomposition is initiated by β-hydride elimination. The influence of fluorine is the same as that observed in the case of ethoxide decomposition. Careful kinetic measurements indicate that the barrier increases from 12 kcal/mole in propyl to 21 kcal/mole in trifluoro-propyl. The reaction is, of course, similar to ethoxide decomposition and one describes the transition state as hydride elimination with charge separation of the form $C^{\delta+}\cdots H^{\delta-}$.

6. Acid Deprotonation on Ag(110) Surfaces

The effect of fluorination of the alkyl chains has a dramatic effect of the surface chemistry of the straight chain acids. The straight chain perfluoro-carboxylic acids are all much stronger acids than their hydrogenated analogues. The pK_a of trifluoro-acetic acid is 0.23 as opposed to 4.73 for acetic acid itself. The net effect on their surface chemistry is to facilitate deprotonated. Acetic acid adsorbed on the clean Ag(110) surface will desorb at 185 K without any decomposition. It is only possible to deprotonate it by adsorbing it on a pre-oxidized Ag(110) surface on which oxygen atoms will serve as a base to deprotonate the acid to form the acetate and water. By comparison the fluorinated acids are all irreversibly adsorbed on the clean Ag(110) surface to form the perfluoro-carboxylates. Whereas, acetic acid desorbs at 185 K, trifluoro-acetic acid forms that acetate on both the clean and pre-oxidized surface. The acetate decomposes at 600 K to yield CO_2 and CF_3 groups.



7. Fluorinated Ethers on the Cu(111) Surface

The chemistry of perfluoro-dioxolane (CF_2CF_2-O-CF_2-O) on the Cu(111) surface has been studied using both thermal desorption methods and vibrational spectroscopy. This molecule was provided by the tribology group at the Wright-Patterson AFB and is a model for some of the PFAE fluids. It is of particular interest because it contains the -O-CF_2-O- linkage which is considered to be the weak link in the Fomblin fluids. It is thought to be the point at which decomposition is initiated at high temperatures thus limiting the thermal stability of the fluid. Thermal desorption reactions on the Cu(111) surface indicate that the model dioxolane is fairly stable, adsorbing at low temperatures and desorbing intact at 110K. The HREELS spectrum of the adsorbed molecule is extremely simple exhibiting only one vibrational mode, the CF stretch at 1250 cm^{-1}. The simplicity of this spectrum suggests that the molecule is lying flat against the Cu(111) surface. In this configuration many of the modes that one might expect to observe have moments parallel to the surface

and as a result are not detected.

There are a couple of explanations for the lack of surface chemical activity of the perfluoro-dioxolane. The first is simply that because of its relatively low molecular weight when compared to the real fluids the barrier to desorption is lower than the barrier to decomposition. The Fomblin fluids will react in the presence of iron surfaces at 600K, decomposing to yield OCF_2 and other products. Because of its low molecular weight the perfluoro-dioxolane desorbs at a much lower temperature and as a result is unable to react. It is possible that decomposition will occur on metal surfaces on which the heat of adsorption is greater than on Cu(111). We intend to explore this possibility by working next with Ni surfaces.

A second possible reason for the lack of activity of the perfluoro-dioxolane is that its propensity to adsorb with its ring parallel to the surface may well mean that there is little interaction between oxygen and the surface, or at least that it is much different from the interaction between oxygen and surface that occurs in the linear chain of the Fomblin molecule. If this is the case then no changes in the surface will allow us to study fluoroether decomposition mechanisms using this particular model compound. Work with other fluorinated ethers is currently underway.

8. Interfacial Lubrication by Model Boundary Layer Films

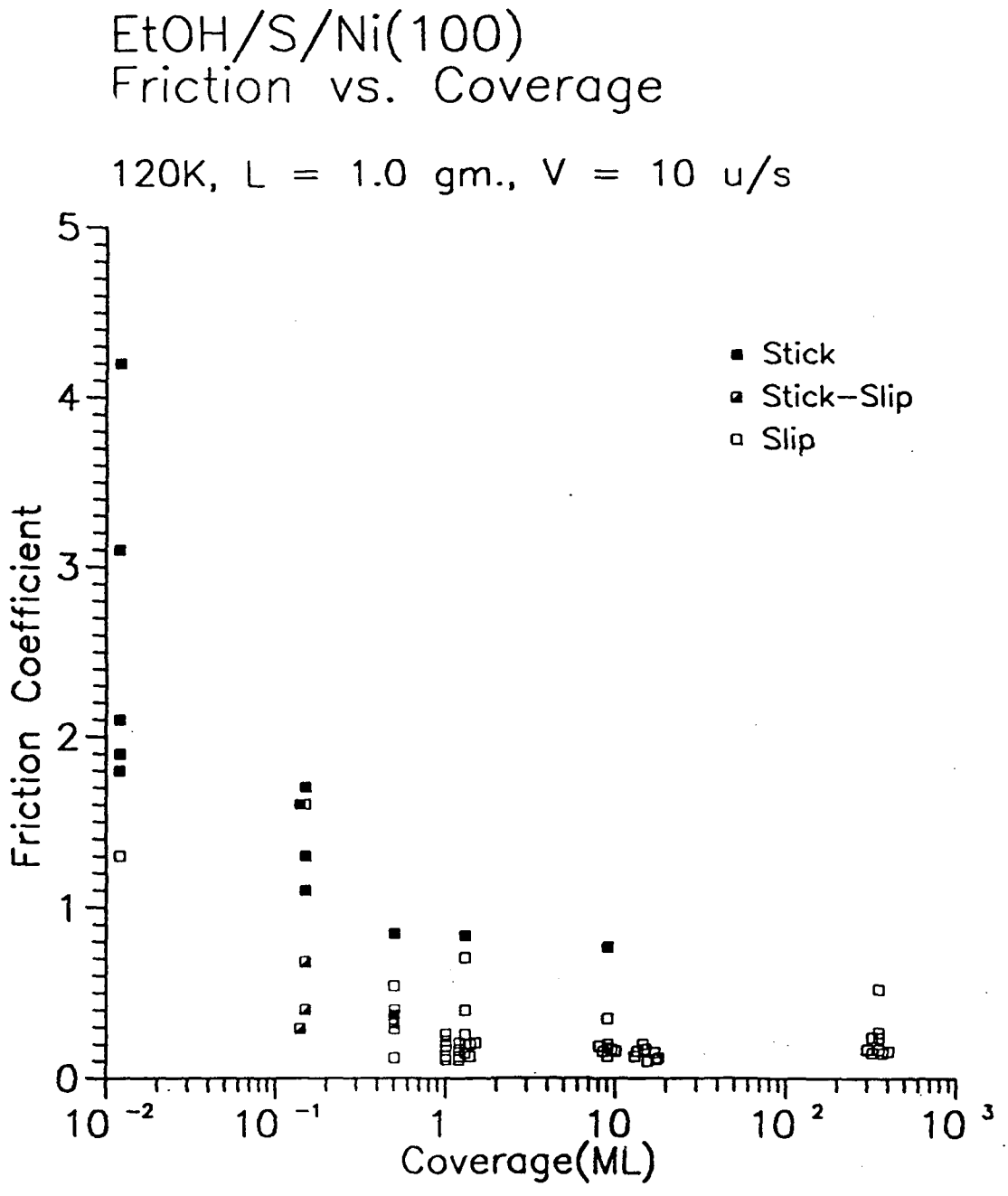
We have learned to make measurement of interfacial friction between surfaces prepared and characterized under UHV conditions. The device used for these measurements has been described in the previous report and is installed in one of our UHV chambers. It allows us full surface preparation capability on two single crystal surfaces, including the ability to heat and cool both samples. In addition, when the two sample surfaces are brought into contact one is able to measure the forces exerted both normal to the interface and shear to the interface. In particular during sliding of one surface over another one can measure the shear or frictional forces developed at the interface. Our first objective has been to determine the adsorbate film thickness necessary to lubricate a metallic interface.

The surfaces that have been used have been Ni(100) surface sulfided to 1/2 monolayer coverage with the sulfur atoms in a c(2x2) array. These surfaces are fairly easily produced and are stable for long periods of time without requiring repeated

preparation. These surfaces have been modified by adsorption of films of ethanol ranging in thickness from 0 to 300 monolayers. Ethanol adsorbs reversibly at 120 K on this surface and the coverage can be determined by examination of the desorption spectrum. The surfaces have then been brought into contact and sheared with respect to one another. We observe three distinct types of behavior during shearing. In the simplest case one surface slides with respect to the other, a constant shear force is developed and the interface has a well defined coefficient of friction. In other cases one observes slip-stick behavior in which one surface adheres to the other until some interfacial shear yield stress is developed and the interface is fractured. In the third case the two surface adhere and one observes very high shear forces. The coefficient of friction is not well defined in this case but the ratios of shear to normal forces tend to be high (in excess of one).

Fig. 3 plots the results of a series of measurements of friction between two surface modified by alcohol films in the coverage range 0 - 300 monolayers. All three forms of sliding behavior described above are observed and are indicated with different symbols on the graph. It is quite clear that above one monolayer ethanol coverage the interface does indeed have a well defined coefficient of friction of 0.22 ± 0.07 and that this is independent of coverage. As the coverage drops below one monolayer it is also clear that the coefficient of friction increases and that the frequency with which the surface stick jumps abruptly. With no ethanol on the surface the coefficient of friction is not well defined but the numbers range from 1 - 5. This is a clear demonstration that one can indeed modify surface mechanical properties with a single monolayer of adsorbate. It is an interesting result in that it is clear that the contact between the two surfaces is neither elastic or reversible. Contact between two metal surfaces under loads of 1 gm. will result in plastic deformation of the material at the points of contact and yet it is apparent that in the contact zone there is a metal-metal interface modified by the presence of the ethanol film initially adsorbed on the two surfaces. In attempts to use different adsorbates we measured coefficients of friction with both hydrocarbon and fluorinated alcohols.

Fig. 3



Coefficients of friction measured at interfaces between Ni(100)-c(2x2)-S surface modified by adsorption of ethanol at coverages from 0 - 300 ML. Three types of sliding behaviour are indicated. At coverages above one monolayer the interface slips with a coefficient of friction of 0.21 $\pm$ .07. T - 120K, Load - 10 mN, Vel. - 10 μm/sec.

TABLE V. Coefficients of Friction Ni(100)/S
Load - 1.0 gm, Vel. - 10 μ/sec., T - 120K

Adsorbate	Coefficient of Friction
C_2H_5OH	0.23 $\pm$ .07
C_4H_9OH	0.35 $\pm$ .07
CF_3CH_2OH	0.40 $\pm$ .07
$C_3F_7CH_2OH$	0.29 $\pm$ .12

It is possible to observe significant differences between surfaces modified by different adsorbates. At this point however the variance in such measurements is still large, possibly due to variance in surface morphology. This is being examined in an effort to obtain more accurate numbers.

9. Publications

1. R. Zhang, A.J. Gellman, "Straight-Chain Alcohol Adsorption on the Ag(110) Surface", *J. Phys. Chem.* 95, (1991) 7433-7437

2. Q. Dai, A.J. Gellman, "HREELS Study of Straight-Chain Alcohols and Alkoxides on the Ag(110) Surface" *Surf. Sci.* 257, (1991) 103-112

3. A.J. Gellman, "Lubrication by Molecular Monolayers at Ni-Ni Interfaces", *J. Vac. Sci. Technol.* A10(1), (1992), 180-187

4. Q. Dai, A.J. Gellman, "Fluorinated Alcohols on Clean and Pre-Oxidized Ag(110) Surfaces: HREELS and TDS Studies" *J. Phys. Chem.* 95, (1991), 9443-9448

5. B. Parker, R. Zhang, Q. Dai, A.J. Gellman, "The Influence of Fluorination on Boundary Layer Surface Chemistry", Surface Science Investigations in Tribology: Experimental Approaches ed. Y. Chung, A.M. Homola, G.B. Street, ACS Symp. Series 485, (1992), p. 181-194

6. A.J. Gellman, Q. Dai "The Mechanism of β-Hydride Elimination in Adsorbed Alkoxides", *J. Am. Chem. Soc.* 115, (1993), 714-722

7. Q. Dai, A.J. Gellman, "Fluorine Sustituent Effects in Alkoxide Chemistry on the Cu(100) Surface" in press *J. Phys. Chem.*

8. B. Parker, A.J. Gellman, "Orientation and Chemistry of Alkyl Thiolates on the Ni(100) Surface" *Surf. Sci.* 292, (1993), 223-234

9. Q. Dai, A.J. Gellman, "Surface Chemistry of Fluoro-Alkoxide Boundary Layer Films", in preparation

10. J. Forbes, A.J. Gellman, "The β-hydride Elimination Mechanism in Adsorbed Alkyl Groups" *J. Am. Chem. Soc.* 115, (1993), 6277-6283

11. B. Parker, A.J. Gellman, "Interactions of Hydrocarbon and Fluorocarbon Acids with the Ag(110) Surface" in preparation

12. P. Cremer, A.J. Gellman, "Substituent Effects on the Transition State for Alkyl Coupling on the Ag(111) Surface", submitted to *Langmuir*

13. A.J. Gellman, "Transition States in Surface Chemistry: Fluorine Substituent Effects", in preparation